Highly efficient blue polyfluorene-based polymer light - emitting diodes through solvent vapor annealing

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Abstract

A highly efficient blue polymer light emitting diode based on [poly(9,9-di(2-(2-(2-methoxy-ethoxy)ethoxy)ethyl)fluorenyl-2,7-diyl)] (PFOEO3) by solvent vapor annealing the polymer emitting layer is fabricated in a bi-layer device with the Al cathode. High electroluminescent efficiency is achieved by balancing charge injection. Better contact interface between polymer and cathode formed by making chain conformation reoriented with solvent vapor exposure. The effect of solvent vapor exposure on the potential barrier height of the interface is estimated using the Richardson-Schottky model. The maximum efficiency achieved 2.3 cd/A of the vapor exposed device from 0.9cd/A of the untreated pristine device.

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1.Introduction

Conjugated polymer electroluminescence (EL) has been extensively studied for its applications in optoelectronic devices since the original report by Burroughes et al.[1] The solution based fabrication process for the polymer organic light emitting diode (OLED) has been recognized as a major advantage compared to the vacuum deposition process for small molecule OLED device. However, one major problem faced in the development of polymer light-emitting diodes is that of unbalanced carrier transport. One option is to use multi-layer devices with charge-injection or transporting layer. One limitation imposed by the solution process is layer mixing during the coating process for multilayered devices. One strategy is to render the layer insoluble by chemically crosslinking prior to the application of the next layer. However this approach not only drives up the cost but also in many cases is impractical. A widely used method is the use of a non-mixing solvent for each layer, such as aqueous suspension of poly(3,4-ethylenedioxythiophene):poly(sodium 4-styrenesulfonate) (PEDOT:PSS) for the hole injection layer and an organic based solution for light emitting layer. However, it is impossible to find a solvent system that does not affect the aqueous deposited layer and the organic solution deposited layer for additional solution based deposition. Therefore most of the practical polymer devices are bilayer device with a hole transport PEDOT:PSS layer and light emitting layer. Hence, there is currently no practical strategy to improve the electron injection for a given light emitting polymer system other than using a low work function cathode, such as alkaline earth metals.

Among the large class of semiconductive organic conjugated polymers, polyfluorene (PFO) and its based copolymers are the most promising for electroluminescent

applications.[2-5] Besides the excellent optical properties and suitable HOMO/LUMO energy levels, PFOs possess excellent charge-transport properties, with hole mobility (10^{-4} cm^2/Vs) more than an order of magnitude higher than that of the poly(p-phenylenevinylene) (10^{-5} cm^2/Vs).[6-9] However, they still suffer from low EL efficiency due to the imbalance of charge carriers. The electron mobility and injection is much more critical than those of holes.[10] Therefore improved electron injection is critical to improving the efficiency of the PFO based OLED device.[11] The arrangements of the side chain and conjugated backbone significantly affects the interfacial characteristics.[12-14] Here, the aim of this work is to modify the interface of the light emitting polymer film and cathode to significantly improve the performance of an OLED device by solvent annealing technique. This technology is not only conformable to solution based process but also adaptable to roll-to-roll production method. We suggest that the solvent vapor approach is a general and cost-effective method of improving the colour purity and efficiency from polyfluorene-based light emitting devices. The reorientation of polymer chains improves the electron injection at the polymer cathode interface but also roles as holes trap to balance the charge injection. The resulting device has an enhanced efficiency of 2.3 cd/A at 6 V from 0.9 cd/A for the pristine device. Such performance is already among the highest ever report of polyfluorene homopolymers with the single layer with Al cathode.

2. Experimental

The light emitting homopolymer poly(9,9-di(2-(2-(2-methoxy-ethoxy)ethoxy)ethyl)fluorenyl-2,7-diyl) (PFOEO$_3$) with Mw 64,000 Dalton and polydispersity 7.4 was purchased from America Dye Source Inc. The molecular structure

is shown in the inset of Figure 1. $PFOEO_3$ was dissolved in chlorobenzene and spin coat onto the PEDOT:PSS coated ITO glass substrates. The $PFOEO_3$ films were exposed in toluene vapor for 1 hour and 5 hour respectively at 25 °C. Aluminum (Al) layer were evaporated on the PFO film surface under a base pressure of 10^{-6} Torr. The final OLED device configuration is ITO/PEDOT:PSS/PFOEO$_3$/Al. *J-V* characteristics were measured using Keithley 2420 source-measure unit. Luminance measurements were performed using a LS-110 model Minolta luminance meter.

3. Results and dission

Figure 1 shows the Brightness-Voltage characteristics of the bilayer polymer OLEDs of the untreated device and two vapor annealed devices. The device fabricated with untreated PFO film is designated as pristine device. The brightness of the devices at the same driving voltage is very dependent upon the annealing conditions, demonstrating that the longer the vapor annealing time, the higher the brightness at a given voltage. The pristine device shows 925 cd/m^2 at 8V, whereas 1356 cd/m^2 and 1498 cd/m^2 under the same voltage when the films were annealed in toluene vapor for 1 hour and 5 hours, respectively. It is found that the turn-on light-emission voltages of the vapor annealed devices are lower than that of the pristine device.[13] The device that was vapor annealed for 5 hours with the Al cathode shows a maximum luminous efficiency of 2.3 cd/A at 6 V, much higher than 0.9 cd/A of the pristine device at 7.5 V as shown in Figure 2. This performance is among the most efficient blue PLEDs based on polyfluorenes. This implies that vapor annealing may facilitate the efficient electron injection at PFO/Al interface, since the film surface was affected by the solvent annealing before Al evaporated. It was found that there was some redshift of PL spectra of the vapor

annealing devices.(fig.S1). Reorientation of polymer chain might make the polymer film more orderly so as to introduce redshift of PL spectra, which might be another reason to increase the efficiency.

Measurement of the current density-voltage (J–V) (J = I/(device area)) characteristics of OLED devices is the general method used to study various injection and transport mechanisms in different device configurations. The J–V characteristics of OLED devices strongly depend on various physical parameters (type of electrodes, active-layer thickness and structure, applied field, temperature, morphology, etc.) In this work we focus on the interfacial properties region of the J–V curve, reflecting the cathode/Al interaction. Electron and hole injections are controlled by the height of the potential barriers of the interface, Φ_B, defined by the difference between the work function of the metal and the highest occupied molecular orbital (HOMO) of the light emitting polymer, and between the ITO and lowest unoccupied molecular orbital (LUMO) of the hole transporting layer, respectively.[15,16] If there is a significant difference in the Φ_B for the two interfaces, the smaller of the two barriers initially controls the J–V characteristics, and the larger one controls the J–V characteristics in the EL condition.[17] In our case, the energy level of HOMO of PFO and PEDOT:PSS are 5.8 eV, 5.2 eV, respectively. LUMO of PFO is 2.6 eV and the work function of Al is 4.1 eV. The J-V curves (Figure 3) of the three different devices can be divided into 3 distinct regions of the applied potential based on the charge transport properties in the PFO layer. Since the injection barrier between Al and PFO for electrons is larger than that between PEDOT and PFO for holes. Holes were injected into the emission layer at the initial potentials, it is region 1. It should be noted that regions 1 doesn't show associated measurable EL

emission because of the low carrier-injection density. As the applied voltage is increased into region 2 when electrons meet with holes initially, unless an appreciable number of holes overcome the barrier height between Al and the LUMO of the active layer, no measurable emission is detected. We therefore focus our attention on region 2 whose change could reflect the electron-injection at the interface of polymer and cathode since we modified the surface by vapor annealing. The result shows that light turn-on voltages of vapor annealed devices are lower than that of the pristine device with the demonstrated result that the longer the annealing time, the brighter the device at a given voltage. The increase in brightness is impliedly attributed to the change on the PFO/Al interface due to the solvent vapor annealing.

We have estimated the reduced energy barrier for electron injection at the cathode by the Richardson-Schottky (RS) model based on the experimental data. In the reported devices, the electron injection barrier between $PFOEO_3$ and Al (~1.5 eV) is much higher than that at the anode for holes (~0.6 eV). Therefore the initial charge inject in region 1 of Figure 3 is mainly due to hole injection from the anode. We mainly estimated the barriers using the data from region 2 whose change could reflect the electron-injection at the interface of polymer and cathode when electrons meet with holes initially. Region 2, the nonlinear portion of the *J-V* curve of Figure 3 (insert), is a consequence of the difficulty of injecting electrons through the junction barrier at the cathode of the device. In region 2 the character of the *J–V* curve is completely dominated by the barrier potential at the cathode. When the applied voltage is increased, exceeding the required energy to overcome the potential barrier, the *J–V* curve in region 3 is dominated by space charge limited current with a trapping mechanism. Therefore, the *J-V* curve characteristic of this

device suggests the current is injection-limited in region 1 and 2, but bulk-limited in region 3. In this case, it is logical to assume that, because of the relatively high barrier between the Al cathode and the PFOEO$_3$, charge transport is considered to be unipolar. The steeper regions 2 of 3-5V in the graphs of Figure 3 correspond to the knee in the *J–V* characteristics, and this is the region where the electron injection through the polymer/Al interface barrier takes place. If the applied voltage exceeds the required energy to overcome the potential barrier, such as 6V, then the *J-V* characteristic is dominated by bulk limited mechanism. The decrease in current density in the annealed sample is implied that charge transport and recombination efficiency of the bulk film are changed by annealing. (Figure 2) It might due to the enhanced injected electrons role as hole-traps in the bulk. The vapor annealing effect on bulk film has been under the further study.

The *J-V* characteristic in region 2 would be continuously influenced by the barrier potential. Electron injection can occur either by thermionic emission or tunneling in the situation studied. However, thermionic emission may play some role at room temperature and the tunneling model does not fit our data very well. Therefore, we focus our attention on regions 2 where EL emission associated with the carrier injection.[18]

$$J = A * \exp\left(\frac{-\Phi_B - \sqrt{e^3 F / 4\pi\varepsilon_0\varepsilon_r}}{kT} \right) \qquad \text{(Equation 1)}$$

Where Φ_B denotes the energy barrier at the metal-polymer interface. *F* is the applied electric field ($F = V/d$ where *d* is the active-layer thickness). *T* is temperature, *k* is the Boltzmann constant. The coefficient *A** is experimentally found to be significantly smaller for organic semiconductors than expected from RS model. We used its room-temperature value of 10^{11} Am^{-2} in the simulation.[19,20]

Figure 4 shows a plot of *LnJ* versus $F^{1/2}$ with *J-V* data taken from region 2 for all 3 types of devices. From the linear fit of the data for each type of device, the barrier height to electron injection could be obtained. For pristine PFOEO$_3$ device, the RS model calculation barrier height is 1.25 eV, which is close to the expected value of 1.5 eV estimated from the difference between Al work function and the LUMO of PFOEO$_3$. 1.185 eV and 1.097 eV were calculation based on the RS model for the devices vapor annealed for 1 hour and 5 hours respectively. The calculation result also shows solvent annealing decreases the electron injection barrier.

The effect of annealing the PFOEO$_3$ layer can be explained by the chemical structure of the polymer as well as the physical interaction between the polymer and the toluene vapor. Reorientation of polymer chain might make the polymer film more orderly so as to introduce redshift of PL spectra (Figure.5). And it is also possible that the reorientation might change interface dipole which induce vacuum level.PFOEO$_3$ consists of two components: the conjugated conductive fluorene backbone (π bond) and the flexible non-conductive ethyleneoxide side chains (σ bond).[13,21-23] These side chains do not support charge transport and light emitting characteristics of the polymer but only provide solubility for solution processing. The conjugated fluorene backbones are likely to be parallel to the surface due to solution processing, while the side chains have a more random orientation between each conjugated backbone. Therefore, we could suppose that there are two components in the "effective barrier height," ϕ, of the PFOEO$_3$ and metal contact at the cathode: An intrinsic component, ϕ_i, between the conductive fluorene backbones and the Al cathode, and an extra component, $\Delta\phi$, between the

nonconductive side chains and the Al cathode, therefore $\phi = \phi_i + \Delta\phi$. The extra component is dependent on detailed molecular conformations and local interfacial morphology. The random orientation of flexible side chains can shield the conjugated backbones from intimate contacts with Al cathode.[12] When exposed to non-polar aromatic solvent vapor, there is the tendency for the polar nonconductive side chains to retreat from the surface to expose the conductive polyfluorene backbone. This reorientation of the side chains provides an intimate contact between the polyfluorene backbone and the Al cathode with reduced interference from the side chains reducing $\Delta\phi$. Therefore, the charge barrier between the PFOEO$_3$ and the Al cathode was reduced in the device with solvent vapor annealing and electron-injection was increased. More balanced charge injection enhanced the performance of the device.

4. Conclusion

In summary, we have developed an efficient bilayer polymer OLED by solvent vapor annealing to change the surface morphology of the light emitting polymer. The change of the light emitting polymer surface morphology dramatically improves the electron injection from the Al cathode. The solvent annealing could be a practical approach to significantly improving the polymer based OLED device without change the chemistry of the material. An efficiency of 2.3 cd/A at 6 V was obtained in a simple bilayer device configuration with Al cathode. The enhancement of efficiency was partially attributed to the chain reorientation after solvent vapor treatment which improved the contact of polymer/metal interface and deduced the electron-injection barrier. The effect of the barrier reduction has been estimated using the RS model. There

is other possible that reorientation of polymer chain change the morphology of the polymer film, which increase the efficiency.

Acknowledgments

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Figure Captions

Figure 1: Brightness vs. voltage characteristics of the devices. Inset shows the molecular structure of PFOEO$_3$

Figure 2. Current efficiency vs. voltage of the devices

Figure 3. Current density vs. voltage of the devices in a log-log scale. The inset shows the curve shape on a linear scale

Figure 4. RS plot in region 2 of the devices with various annealing time at room temperature

Figure 5. Photoluminescence spectra of the films with different annealing time

Table Caption

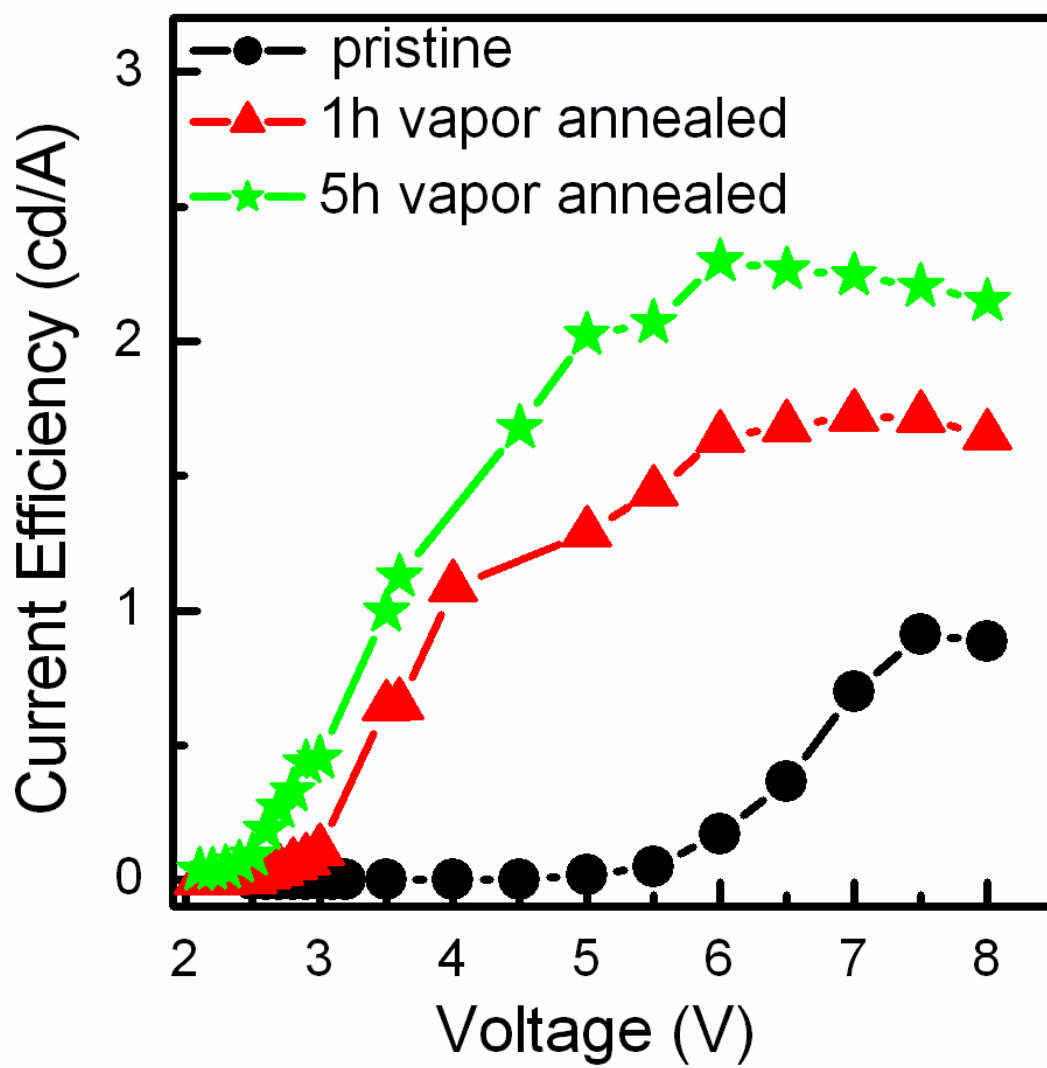Table 1. The RS model calculated electron injection barrier heights.
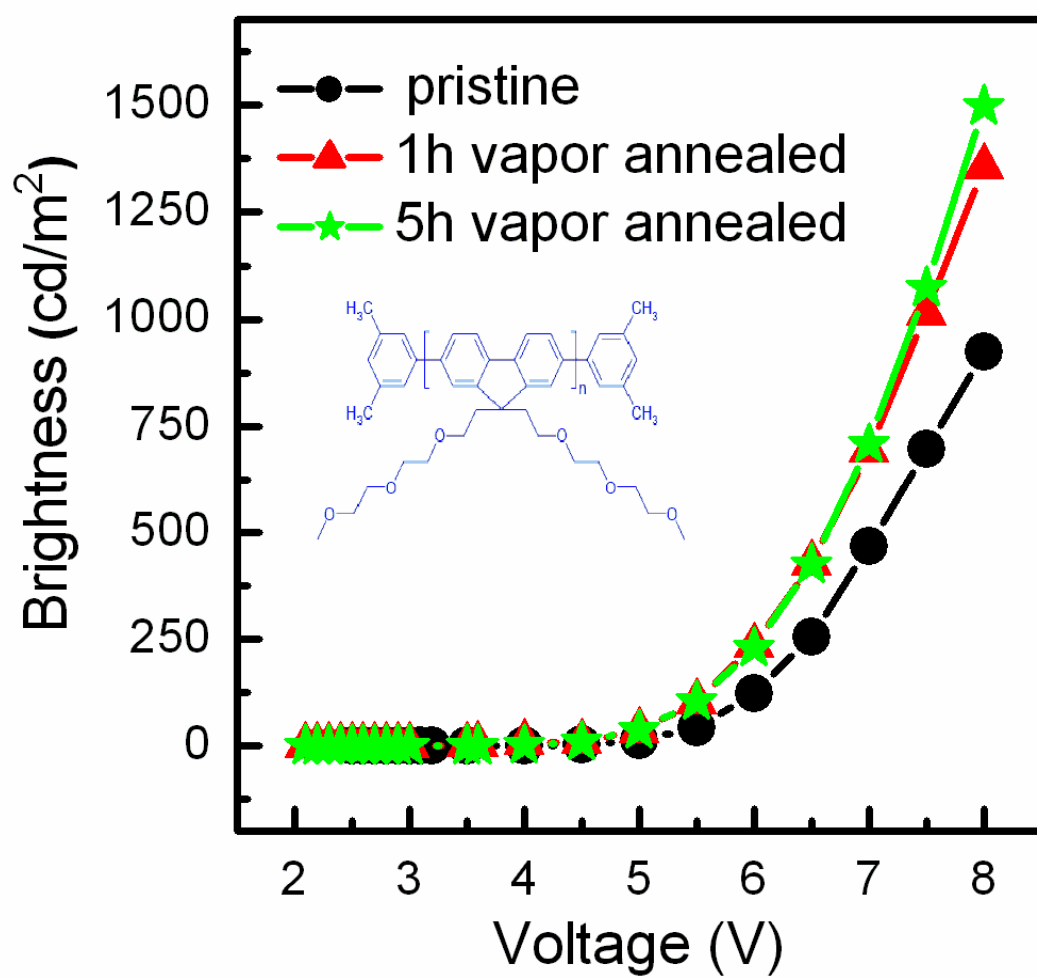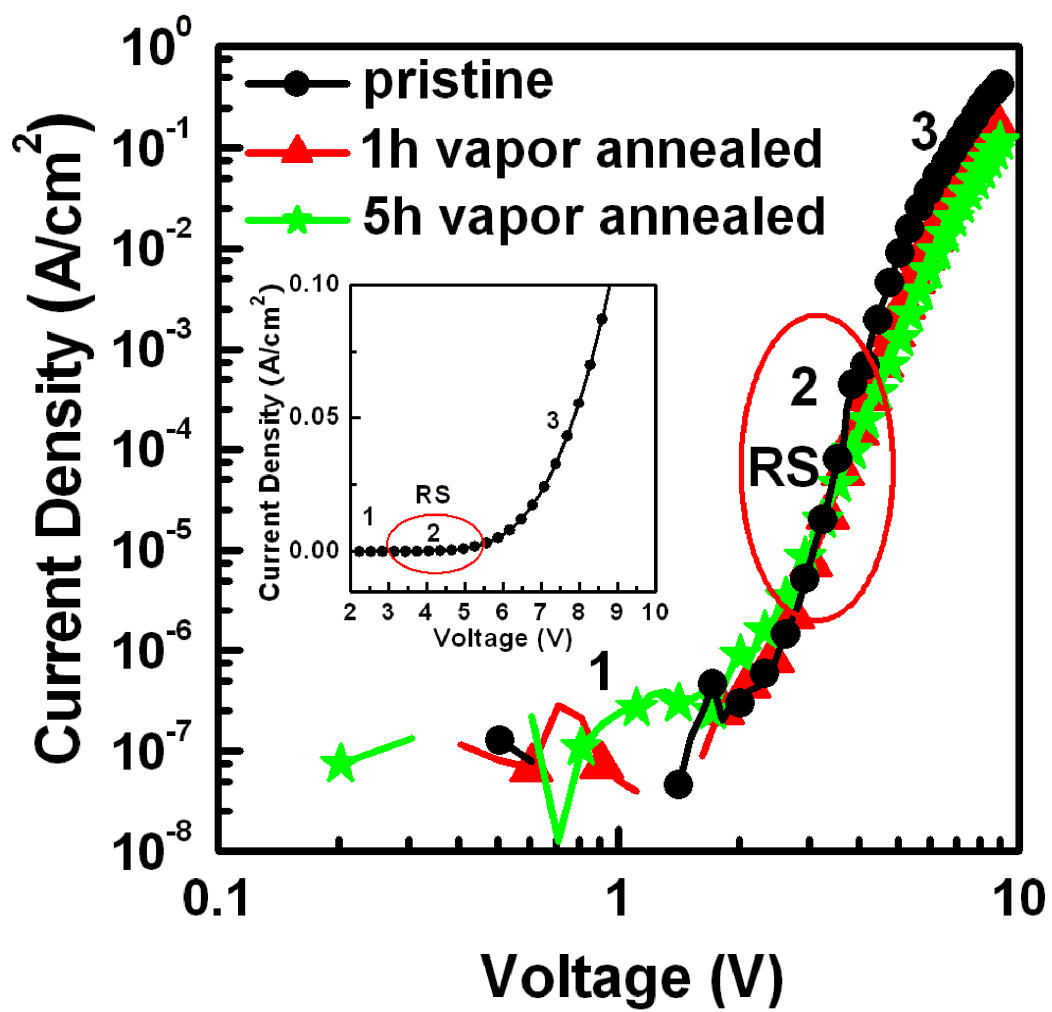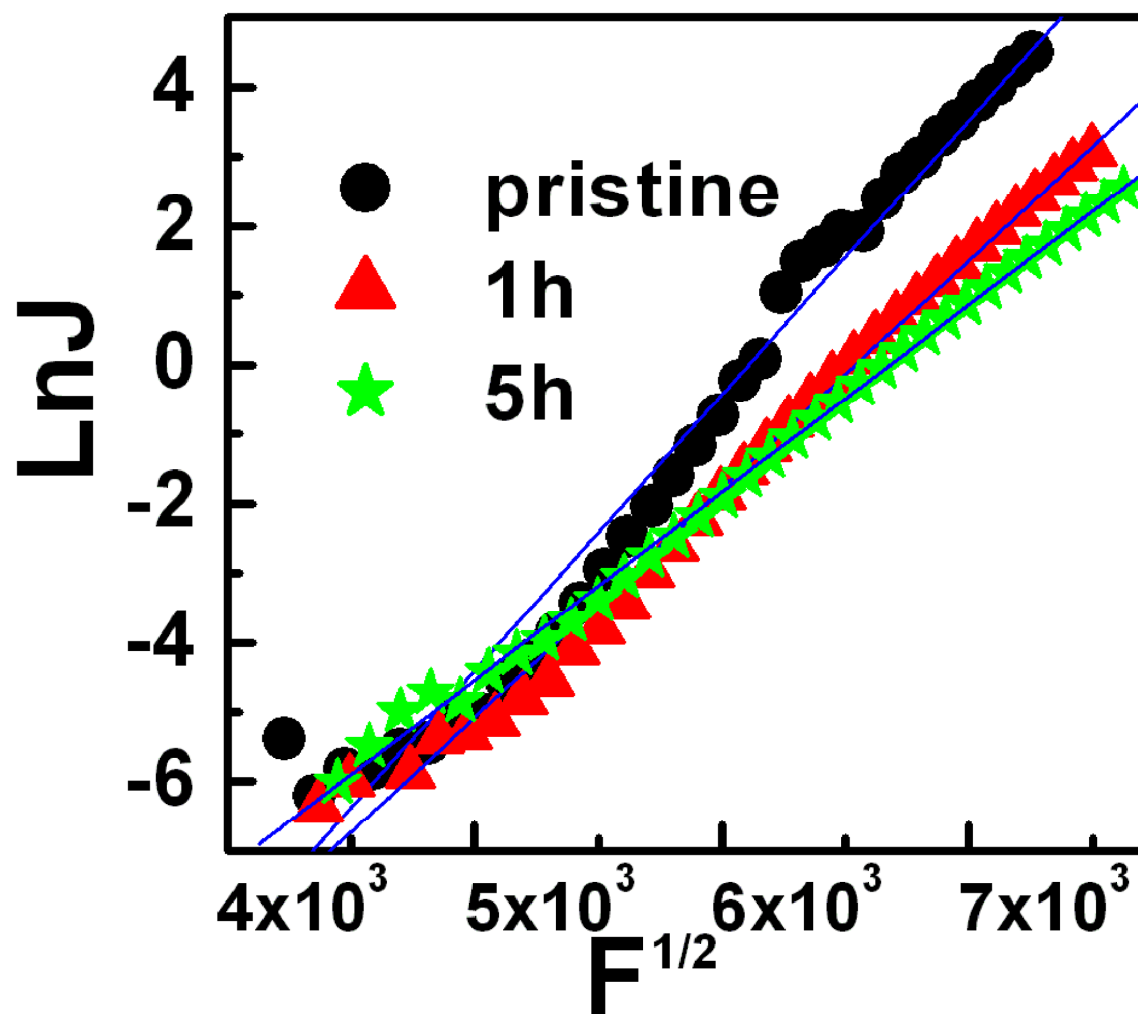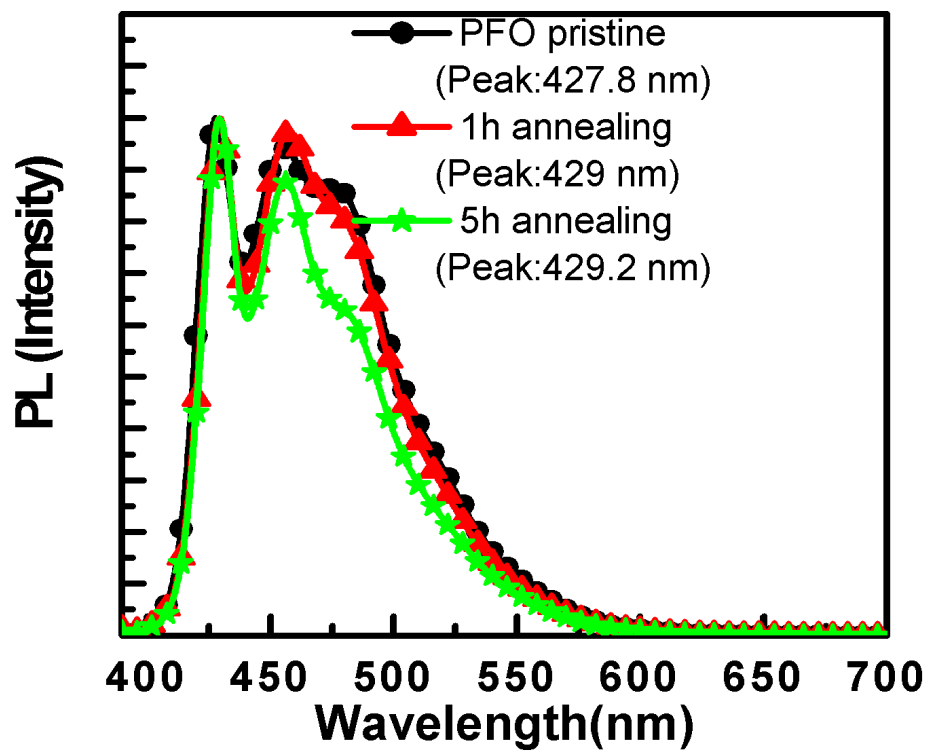
Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Annealing Time (h)	Φ_B (eV)
0	1.25
1	1.185
5	1.097

Table1